

University of Groningen

## Ab initio and work function and surface energy anisotropy of LaB6

Uijtewaal, M. A.; de Wijs, G. A.; de Groot, R. A.

*Published in:*  
Journal of Physical Chemistry B

*DOI:*  
[10.1021/jp063347i](https://doi.org/10.1021/jp063347i)

**IMPORTANT NOTE:** You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
2006

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Uijtewaal, M. A., de Wijs, G. A., & de Groot, R. A. (2006). Ab initio and work function and surface energy anisotropy of LaB6. *Journal of Physical Chemistry B*, 110(37), 18459-18465.  
<https://doi.org/10.1021/jp063347i>

**Copyright**

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

**Take-down policy**

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

*Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.*

# Ab Initio and Work Function and Surface Energy Anisotropy of LaB<sub>6</sub>

M. A. Uijtewaal,<sup>\*,†</sup> G. A. de Wijs,<sup>†</sup> and R. A. de Groot<sup>†,‡</sup>

*Electronic Structure of Materials, IMM, Radboud University, P. O. Box 9010, Nijmegen, NL-6500 GL, The Netherlands, and Chemical Physics Laboratory, MSC, University of Groningen, Nijenborgh 4, Groningen, NL-9747 AG, The Netherlands*

*Received: May 31, 2006; In Final Form: July 25, 2006*

Lanthanum hexaboride is one of the cathode materials most used in high-power electronics technology, but the many experimental results do not provide a consistent picture of the surface properties. Therefore, we report the first ab initio calculations of the work functions and surface energies of the (001), (011), (111), (112), and (012) surfaces by considering the different surface terminations and structural relaxation. Either the (111)B- or the (001)La-terminated surface is the most stable, depending on La chemical potential. The work function of the latter is the lowest (2.07 eV) of the surfaces considered. Both the work function and surface energy decrease further when surface La is replaced by Ba and become, respectively, 1.43 and 7.7 eV/nm<sup>2</sup> at the chemical potentials of elemental lanthanum and barium bulk. These results compare favorably with previous work on the intermetallics BaAl<sub>4</sub>, CaAl<sub>4</sub>, and BaAuIn<sub>3</sub>. Their most stable surfaces possess the lowest work function. Now, we study a compound with a decidedly different crystal type and with its constituting elements from column 3 of the periodic table, of which one is nonmetallic.

## 1. Introduction

Electron-emitting materials are applied in many types of technology. Some examples are vacuum electronic devices such as cathode-ray tubes (CRTs), microwave devices, FELs (free electron lasers), and organic light-emitting diodes (OLEDs). Important desirable properties of a cathode metal are a low work function ( $\Phi$ ) and a high (surface) stability.<sup>1</sup> Ideally, they are combined in one surface of one compound.

A low work function and high (surface) stability are incompatible for elements in general: the element with the lowest work function, cesium (2.14 eV),<sup>2</sup> is highly reactive and possesses a low melting temperature. Noble metals (silver/gold/platinum), on the other hand, are hardest to oxidize, but their (polycrystalline) work function is at least twice as large (4.25/5.1/5.65 eV, respectively).<sup>2</sup> The model of Smoluchowski<sup>3</sup> explains the (surface) anisotropy for the elements well: the surface electrons are smoothed with respect to the bulk termination at an “open” surface, i.e., one with a smaller number of atoms per surface area. As a consequence, a dipole moment builds up that decreases the work function. On the other hand, open surfaces tend to be less stable.

Few results are available on the work functions and the stability of compound surfaces. In previous (theoretical) work,<sup>4,5</sup> we showed that the cationic surfaces of intermetallic compounds with polar unit cells are stable and exhibit the lowest work function. It is even lower than that of the elemental constituents. The difference in electronegativity between the constituting elements lowers both the work function and enhances the stability of the cationic surface. To explore the generality of the effect, a study was initiated on surfaces of LaB<sub>6</sub>.

Lanthanum hexaboride is an excellent thermionic electron emission source with high brightness, low volatility, and long

service life.<sup>6</sup> It functions equally well as a thermal field emitter,<sup>7</sup> and is easy cleavable and stable, even in air.<sup>8</sup> The crystal morphology depends on the preparation conditions: needles, rods, and nanowires are possible with different orientations as well as plates and cubic crystals. The melting point of LaB<sub>6</sub> is 2715 °C, and it is only reactive in the molten state.<sup>9</sup> Lanthanum hexaboride is a purple metal, and its electron conductivity is about 1/5 of that of copper.<sup>10</sup>

The work functions of cubic LaB<sub>6</sub> have been studied intensively, but there is little consensus. Already, before 1976, values ranging from 2.3 up to 3.2 eV were published for the (001) surface according to Yamauchi.<sup>11</sup> Later reports of Aono et al.,<sup>12</sup> Mogren et al.,<sup>13</sup> Marchenko et al.,<sup>8</sup> Waldhauser et al.,<sup>14</sup> and Kawanowa et al.<sup>15</sup> present work functions of, respectively, 2.1, 3.3, 2.5, >2.6, and 2.3 eV.

There is no agreement, either, on the order of the work functions for the different surfaces. Most groups state that  $\Phi_{(001)} < \Phi_{(011)} < \Phi_{(111)}$  (Takigawa et al.)<sup>16</sup> as, e.g., Nishitani et al.:<sup>17</sup> 2.3, 2.5, and 3.3 eV, respectively. This ordering is explained by a surface dipole moment that lowers the work function. Others obtained orderings of 2.68 eV (011) < 2.86 eV (001) < 3.4 eV (111) (Oshima et al.).<sup>18</sup> Nevertheless, some groups present lower work functions for higher index surfaces: • 2.2 eV (012), which is smaller than those of the (001), (011), and (111) surfaces (Oshima et al.),<sup>19</sup> • 2.5 eV (013) <  $\Phi_{(012)} < \Phi_{(001)} < \Phi_{(011)} < \Phi_{(111)} < \Phi_{(112)}$  (Gesley et al.),<sup>20</sup> • 2.41 eV (346), 2.5 eV (001), 2.64 eV (011), 2.90 eV (111) (Swanson et al.).<sup>21</sup> The last group mentioned, however, that much heating was required to get reproducible values. Moreover,  $\Phi_{(346)}$ , as determined by thermionic emission (TE) above 1200 K, agreed poorly with the RT (room temperature) value from the field emission retarding potential (FERP) method.

Conflicting evidence also exists on the temperature dependence of the work function. Fomenko<sup>22</sup> states that, when using the contact potential difference (CPD) method at RT, it is approximately 2 eV and that it increases to about 3 eV at

\* Corresponding author. E-mail: M.Uijtewaal@science.ru.nl.

<sup>†</sup> Electronic Structure of Materials, IMM, Radboud University.

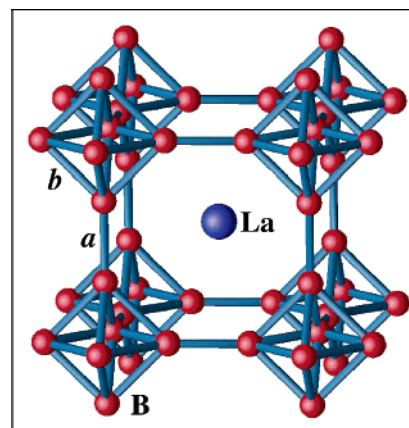
<sup>‡</sup> Chemical Physics Laboratory, MSC, University of Groningen.

1000 K as determined by TE. According to Samsonov et al.,<sup>23</sup> on the other hand, the value is 2.95 eV and it hardly depends on temperature. Kuznetsov et al.<sup>24</sup> even reported that the monocrystalline work function decreases with temperature. They give values of 2.64 eV (001), 2.81 eV (polycrystalline) and 2.76 eV (polished polycrystalline), all at high T. Other work functions obtained for polycrystalline samples by Yutani et al.,<sup>25</sup> Ebihara et al.,<sup>26</sup> and Baikie et al.,<sup>27</sup> respectively, are 2.7–2.8 eV (thin films), 2.68 eV, and 2.55 eV, which rises to 3.65 eV when poisoned with residual gas. Nakamoto et al.<sup>7</sup> use a similar phenomenon (oxidation) to explain the difference between their measured 3.7 eV and the reference value of 2.8 eV. Pelletier et al.,<sup>28</sup> using a Richardson method, also found a polycrystalline work function of 2.70 eV, but that decreases to 2.36 eV when the molybdenum contaminations were removed from the surface. They concluded that the variations in work function are generally caused by surface impurities.

It is interesting to see what more controlled modifications of the surface can do. Chambers et al.<sup>29</sup> report that the work functions of the (001) and (011) surfaces of LaB<sub>6</sub> are both 2.78 eV and that Cs absorption lowers them to, respectively, 1.97 and 1.88 eV. The work function even becomes as low as 1.35 and 1.47 eV, respectively, when there is preabsorbed oxygen present on the surface before the cesium is deposited. Danielsen<sup>30</sup> reported that a thick layer of cesium oxide at LaB<sub>6</sub> causes a work function as low as 1.0 eV and that this layer is stable up to 390 K. By linearly extrapolating his TE results around 1000 K, Fomenko<sup>31</sup> hinted that the work function of a layer of BaB<sub>6</sub> could be as low as 1.38 eV for low temperatures. There is one theoretical paper on the  $\Phi_{(001)}$  of LaB<sub>6</sub> by Monnier et al.<sup>10</sup> According to their DFT calculation, surface atom relaxation lowers the value from 2.45 to 2.27 eV.

There is incomplete knowledge on the stability of lanthanum hexaboride surfaces. Zhang et al.<sup>6</sup> created a nanowire with a [111] growth direction and found that the (001), (011), and (111) planes are the principal terminating facets and thus the most stable ones. It might be concluded from the terminating area sizes that the (001) surface is somewhat more stable than the (011) surface and that the (111) surface is less stable still. The conclusion is supported by the flat termination of nanowires with a [001] growth direction<sup>32</sup> and X-ray diffraction, both on thin films<sup>25</sup> and coatings on molybdenum<sup>14</sup> of LaB<sub>6</sub>. Takigawa et al.<sup>16</sup> found that emission from the [001] cathodes is unstable in contrast with emission from [011] and [111] cathodes. It was explained by evaporation of the (001) surface from the top of the [001] cathode and formation of (001) surfaces on the slope of the [011] and [111] cathodes. Again, the (001) surface is most stable. In addition, Oshima et al.<sup>19</sup> measured the stability of the (012) surface against oxygen chemisorption. It is comparable to that of the (011) surface, but low with respect to that of the (111) and (001) surfaces, though.

A better picture can be given of the structure of LaB<sub>6</sub> surfaces. The (001) surface is unreconstructed and terminated by lanthanum atoms.<sup>15</sup> The top layer is somewhat displaced inward with respect to the bulk positions. Oshima et al.<sup>19</sup> observed a 1 × 1 La structure at the (012) surface, which they modeled with repeated steps of (001) and (011) faces. However, the XPS (X-ray photoemission spectroscopy) results at large angles give more lanthanum than the model can account for. The (111) surface is also unreconstructed, it is supposed to be terminated by B atoms and subsurface La atoms have, most likely, also moved outward. The lanthanums at the (011) surface are displaced outward, but no consensus exists on its reconstruction. Oshima et al.<sup>18</sup> saw (111) facets on the (011) surface (at



**Figure 1.** Simple cubic crystal structure of LaB<sub>6</sub>. Each lanthanum atom is enclosed in a boron cage of 24 atoms.

1400 °C and lower vacuum), and according to Nishitani et al.,<sup>17</sup> there is a  $c(2 \times 2)$  reconstruction caused by the La atoms. Watson et al.<sup>33</sup> analyzed its surface structure and mentioned that the (011) surface appears neither to facet nor to reconstruct, though, in accordance with low-energy electron diffraction (LEED) results of Swanson et al.<sup>21</sup>

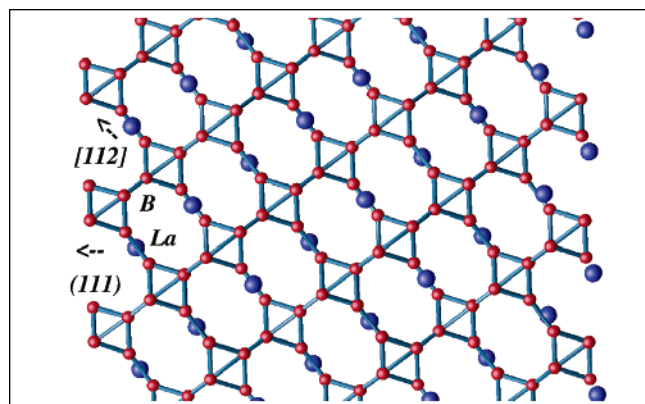
From theory side, Monnier et al.<sup>10</sup> found that (001) La atoms move inward by 6.5% of the lattice constant during structural relaxation, that the relaxation energy is 0.4 eV per surface unit cell, and that there is an 8.4 eV/atom energy difference between the (001)La surface and the (001)B one, with the surface lanthanums removed to the vacuum.

In this paper, the theoretical anisotropy of the work function and surface energy of LaB<sub>6</sub> is reported from ab initio calculations on the (001), (011), (111), (112), and (012) surfaces of lanthanum hexaboride, including the different surface terminations and structural relaxations. No reconstructions are considered, but we did consider [001] steps at the (012) surface and monolayers of Ba and Cs as well as bilayers of La at the (001) and (112) surfaces.

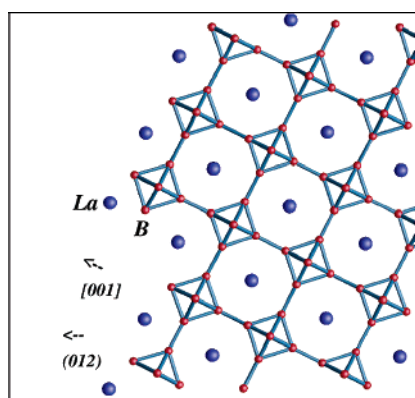
The paper is organized as follows. First, the details of the calculations are given. Next, the crystal and electronic structure are reported. The following section is devoted to the work functions of LaB<sub>6</sub>. After that, the surface stabilities are discussed, and finally, the conclusions are presented.

## 2. Computational Method

The first-principles calculations were carried out using density functional theory (DFT) in the local density approximation (LDA)<sup>34</sup> with generalized gradient corrections (GGA).<sup>35</sup> We used the total energy and molecular dynamics program Vienna ab initio simulation package (VASP),<sup>36–38</sup> which has the projector-augmented-wave method (PAW)<sup>39,40</sup> implemented. Nonlinear core corrections<sup>41</sup> were applied for all atoms. Semicore orbitals of Cs, Ba, and La 5s and 5p electrons were included. The Kohn–Sham orbitals were expanded in plane waves, with cutoffs of 400 eV for the bulk and the (001)La surface calculations and 319 eV for the rest. The Brillouin zones were sampled with 12·12·1 (001), 12·8·1 (011), 8·8·1 (111), 6·6·1 (112), and 8·2·1 (012) Monkhorst–Pack<sup>42</sup> *k* point grids. They had symmetries of, respectively,  $C_{4v}$ ,  $C_{2v}$ ,  $C_{3v}$ ,  $C_1$ , and  $C_{1h}$ , which resulted in 28, 35, 10, 13, and 10 *k* points, respectively, in their irreducible parts. The (periodically repeated) unit cells contained slabs with thicknesses of 4 [(001) boron], 5 [other (001)], 6 [(011) and (112)], and 9 [(111) and (012)] bulk unit cells. Dipole corrections were used for slabs with two different surfaces.



**Figure 2.**  $B_{\text{dip}}$  (left) and  $La$  (right) terminations of the (111) surface of LaB<sub>6</sub>. The [112] direction is also indicated.



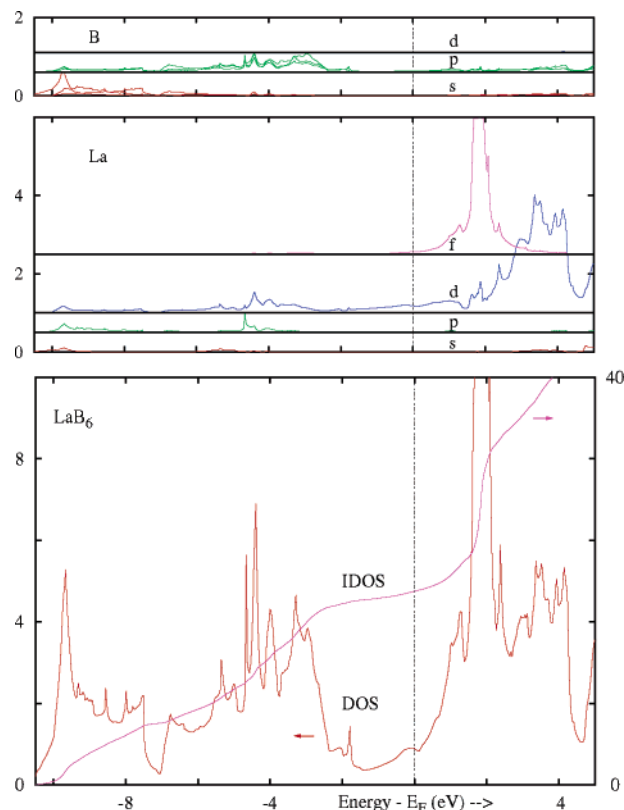
**Figure 3.** Stepped (012) surface (left) of LaB<sub>6</sub>. The [001] direction is also indicated.

### 3. Lanthanum Hexaboride Structure

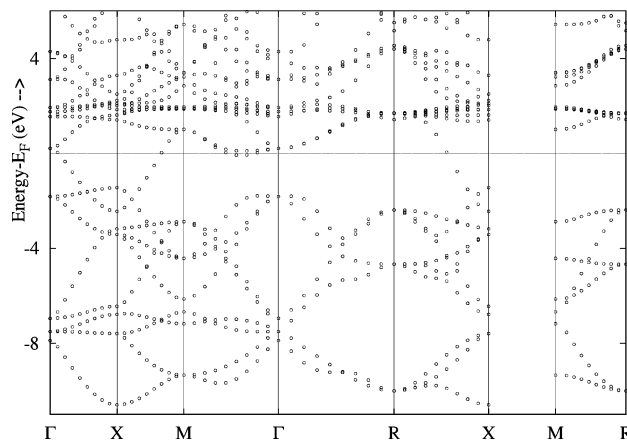
The LaB<sub>6</sub> crystal structure<sup>43</sup> is depicted in Figure 1. It is simple cubic (space group 221), and each La is enclosed in a B cage of 24 atoms that makes for the rigidity of the structure. The lattice constant is experimentally determined at  $c = 4.153$  Å, with a boron positional parameter of  $z = 0.1993$ . Our theoretical values of  $c = 4.145$  Å and  $z = 0.1996$  deviate less than 0.2%. It follows that interoctahedral boron bonds ( $a$  in the figure) are 94% of the length of the intraoctahedral ones ( $b$ ). The binding energy is calculated at 3.96 eV per formula unit with respect to hexagonal lanthanum and  $\alpha$ -rhombohedral boron. It compares well with formation enthalpies given by Topor et al. (−4.15 eV/formula unit)<sup>44</sup> and Meschel et al. (−3.6 eV/formula unit).<sup>45</sup>

The (001), (011), (111), (112), and (012) surfaces are considered in this study. For each direction, one termination is possible with lanthanum atoms (called  $La$ ) and two or three consisting only of boron atoms (see also Figure 2). The latter either form a stoichiometric *slab* by themselves<sup>46</sup> or together with the lanthanum surface. They are called  $B_{\text{stoi}}$  and  $B_{\text{dip}}$ , respectively. The (001) and (112) surfaces with an extra La layer (named  $2La$ ) or with all surface La replaced with Ba ( $Ba$ ) or Cs ( $Cs$ ) are also studied, as well as [001] $La$  steps on the (012) surface. The latter is depicted in Figure 3.

The bulk density of states (DOS), integrated DOS, and partial DOS per atom of are shown in Figure 4. The DOS has a peak at 2 eV above the Fermi level consisting of La  $f$  states. The corresponding band structure is depicted in Figure 5. It compares very well to that of Van der Heide et al.<sup>47</sup> and to the full potential linearized augmented plane waves (FLAPW) LDA bandstructure



**Figure 4.** Density of states (DOS, states/eV/formula unit) of LaB<sub>6</sub> as function of energy relative to  $E_F$ . Integrated DOS (number of electrons) and partial DOS (states/eV/atom) of crystallographic nonequivalent atoms are also plotted. La  $f$  states are scaled down by a factor of 4. The radii used for the atoms are 1.9 Å (La) and .9 Å (B).



**Figure 5.** Band structure of LaB<sub>6</sub> along high-symmetry lines.

from Kubo et al.<sup>48</sup> The main difference is that, in the latter result, the band between M and  $\Gamma$  is not split up.

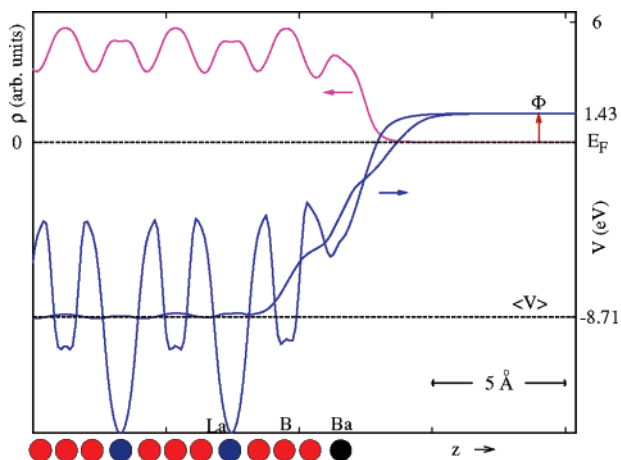
### 4. Work Function

The work function is defined as the minimum amount of energy it takes to extract electrons from a metal, i.e., bring them from the Fermi level ( $E_F$ ) to the vacuum  $V_{\text{vac}}$ .

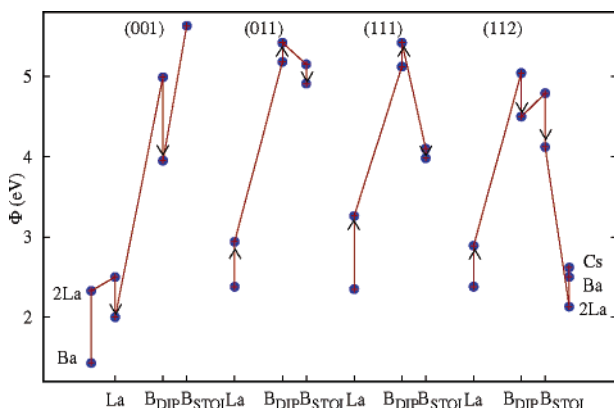
$$\Phi = V_{\text{vac}} - E_F$$

The work function is surface dependent at locations that are microscopically far from the material but macroscopically near. The work function at the large distance then is an average over the various surfaces.<sup>49</sup> A bulk calculation provides an accurate  $E_F$ . It can be compared with the vacuum potential of a





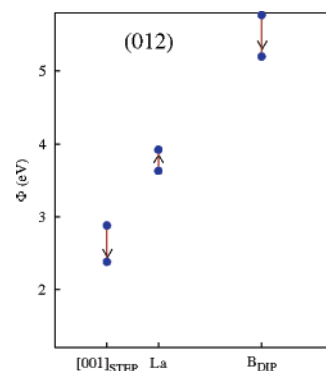
**Figure 6.**  $\text{LaB}_6$  (001) surface with a monolayer Ba on top. The charge density ( $\rho$ , arbitrary units) and electrostatic potential ( $V$ , eV relative to  $E_F$ ) are laterally averaged and plotted as a function of position perpendicular to the surface ( $z$ ). The potential is, for each  $z$ , also averaged over a bulk unit cell. Layers of La, B, and Ba are indicated with blue, red, and black circles, respectively. The average bulk potential is  $-8.71$  eV. The work function ( $\Phi$ ) results in  $1.43$  eV.



**Figure 7.** Work functions ( $\Phi$ , eV) of the  $\text{LaB}_6$  surfaces. Arrows indicate the effect of structural relaxation. No arrow means that only the work function of the relaxed surface is plotted. Names of the surfaces are explained in the text. Lines connect the data points. The lowest work function value ( $1.43$  eV) is for the (001) surface with a monolayer Ba on top.

calculation with a slab of material in the supercell by means of the average (electrostatic) potential in a bulk unit cell ( $\langle V \rangle$ ). The procedure is outlined in Figure 6. Ten Å of empty space suffices for the potential to converge to its vacuum value. The work function of the surface shown is  $1.43$  eV. Accuracies better than a tenth of an eV can be achieved with moderate slab widths.<sup>50</sup>

Figure 7 displays the work functions of the surfaces considered. The names are explained in the previous section.  $\text{LaB}_6$  surfaces containing La possess the lowest work function for each direction, and surprisingly, those are all about  $2.4$  eV. Except for the (001) surface, the work functions increase considerably by structural relaxation. This can be attributed to the relatively small amount of (La) atoms per surface area for these surfaces. The lanthanum atoms then move inward during relaxation, and so boron atoms come closer to the surface. The ionic surface dipole that decreases the work function is reduced. The opposite reasoning explains that adding an extra La layer to the (112)La surface decreases the work function considerably, as this increases the surface atom density. Both the amount of relaxation is reduced, and the ionic surface dipole is increased. Substitution of surface lanthanum with Cs or Ba atoms does not quite have this effect. We get an idea of the size of the



**Figure 8.** Work functions ( $\Phi$ , eV) of the  $\text{LaB}_6$  (012) surfaces terminated by lanthanum, by boron, and by [001] steps, as explained in the text. Arrows indicate the effect of structural relaxation.

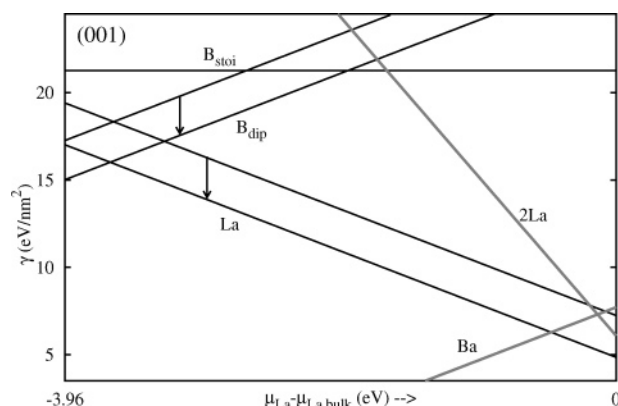
ionic surface dipoles by comparing the work function of La surfaces with those for (0001) and (0120) surfaces of elementary lanthanum. Calculations show that they are  $3.13$  and  $2.92$  eV, respectively, and that ionic dipole moments are considerable.

Lanthanum atoms at the (001)La surface relax no less than  $0.3$  Å inward, in good agreement with Monnier et al.<sup>10</sup> However, the effect of relaxation on our work function ( $2.50$  eV decreases to  $2.07$  eV) is a little larger than what they find. Moreover, the effect is opposite to that at the other surfaces, where the work functions increase, because the lanthanum density at the (001) surface is larger. The inward movement of surface atoms now increases the ionic dipole moment because the remaining electrons of the La atoms can then participate in a surface state with the B atoms, as observed by angle-resolved UPS<sup>51</sup> and shown by Monnier et al.<sup>10</sup> We also find this surface state. The increased density of atoms at the surface also makes that addition of an extra layer of La at the (001) surface *does not* decrease the work function, but replacing the original (surface) lanthanum with barium does, even to a astonishingly low value of  $1.43$  eV. The value agrees very well with the work function of a layer of  $\text{BaB}_6$ , as hinted by Fomenko.<sup>31</sup>

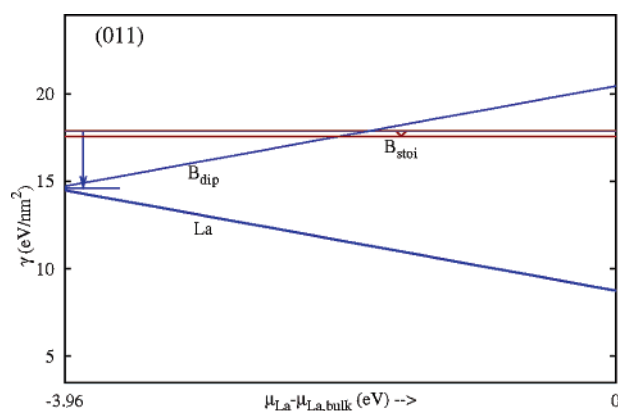
The work functions of the boron-terminated surfaces range from less than  $4$  eV to nearly  $6$  eV and also the effect of relaxation greatly varies: work functions mostly decrease, that of the (001)  $B_{\text{dip}}$  surface even by  $1$  eV, but e.g., the work function of the (011)  $B_{\text{dip}}$  surface increases by a few tenths of an electronvolt. On one hand, an increase is expected from the Smoluchowski rule: relaxation “closes” the surface and reduces the smoothing of the electrons. An open B-terminated surface neighboring a La layer, on the other hand, would show a decrease because relaxation then makes lanthanum atoms move closer to the surface and thereby decreases the ionic surface dipole moment. These considerations explain the relaxation effects for all but the (001)  $B_{\text{dip}}$  surface. At that surface, the outer B layer moves in by  $0.2$  Å and so flattens the octahedra of which it is part. Apparently, the ionic surface dipole decreases exceptionally.

We conclude with the (012) surface. It is a good example of a higher index surface for which the Smoluchowski rule predicts a decreased work function *and* stability. Moreover, Gesley et al.<sup>20</sup> and Oshima et al.<sup>19</sup> even reported that its work function is lower than that of the (001) surface. Therefore, it makes for a good test case both to estimate the relevance of the results on low index surfaces and to check the appropriateness of the old rule, as this is a quite open surface.

Our calculations show that the work function of the (012) La termination is  $3.63$  eV and that relaxation increases it to  $3.92$  eV. The  $B_{\text{dip}}$  termination is even more dramatic: it



**Figure 9.** Surface energies ( $\gamma$ , eV/nm<sup>2</sup>) of the (001) surfaces as function of the La chemical potential ( $\mu$ , eV). It ranges from the potential of La bulk to that minus the binding energy of lanthanum hexaboride. Surface names are explained in the text. The arrows indicate the effect of relaxation for two of the surfaces. For the others, only the energy of the relaxed surface is plotted. (001)La is the most stable one. However, in nearly the whole range of the chemical potential, the Ba surface is even more stable.



**Figure 10.** Surface energies ( $\gamma$ , eV/nm<sup>2</sup>) of the LaB<sub>6</sub> (011) surfaces as a function of the lanthanum chemical potential ( $\mu$ , eV). It ranges from the potential of La bulk to that minus the binding energy of lanthanum hexaboride. Surface names are explained in the text. The arrows indicate the effect of relaxing the stoichiometric slabs, possibly terminated by different surfaces. The (011)La surface is the most stable one.

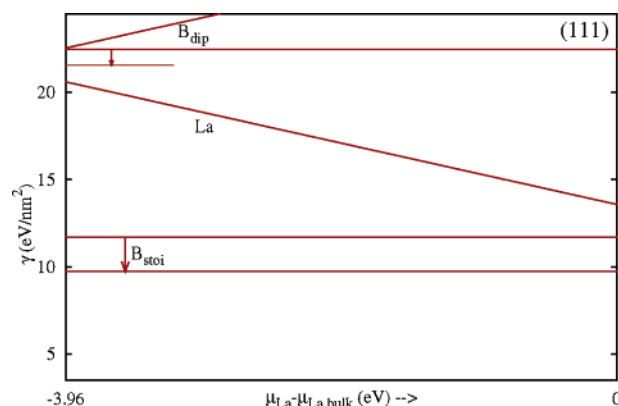
possesses a work function of 5.20 eV (5.77 eV before relaxation). The Smoluchowski model cannot explain these results.

The enormous discrepancy between the measured and the calculated (012) work function could be resolved by considering steps on the (012) surface. Oshima et al.<sup>19</sup> proposed a model of repeated [001] and [011] faces. Their model, however, cannot fully account for the amount of lanthanum as seen by XPS, and the (011) work function is quite a bit larger than that of the (001) surface. Therefore, we consider only steps of [001] faces. These steps do decrease the work function considerably, to 2.88 eV before and 2.38 eV after relaxation, but it is still above the (001) one. The results are displayed in Figure 8.

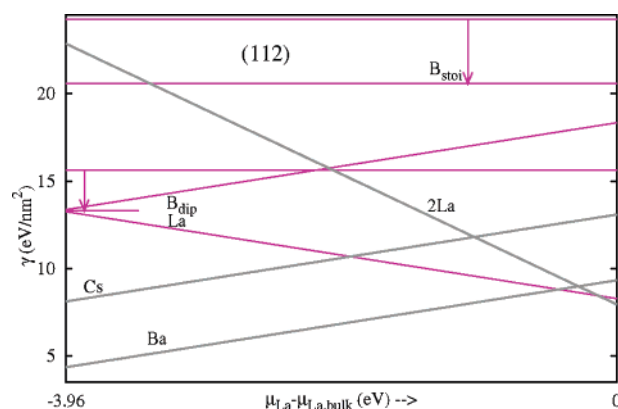
This surface already shows rather extreme behavior but does not improve on the results of the surfaces of lower index, and so we presume that it is not necessary to study surfaces of even higher index.

## 5. Surface Stability

The stability of a surface is a complex notion. It not only depends on the (initial) surface energy ( $\gamma$ ), but also on the energy



**Figure 11.** Surface energies ( $\gamma$ , eV/nm<sup>2</sup>) of the LaB<sub>6</sub> (111) surfaces as a function of the La chemical potential ( $\mu$ , eV). It ranges from the potential of La bulk to that minus the binding energy of lanthanum hexaboride. Surface names are explained in the text. The arrows indicate the effect of relaxing the stoichiometric slabs, possibly terminated by different surfaces. The (111)B<sub>stoi</sub> surface is the most stable one.



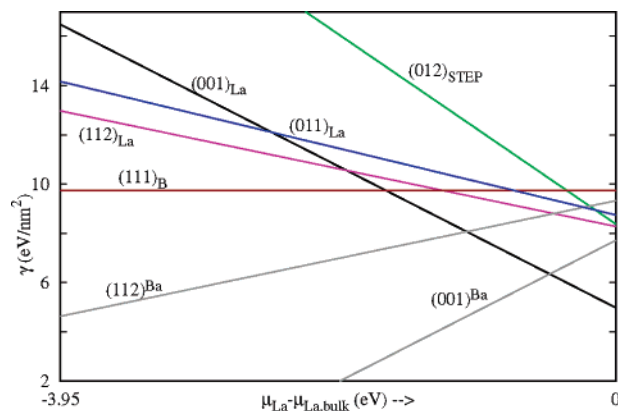
**Figure 12.** Surface energies ( $\gamma$ , eV/nm<sup>2</sup>) of the (112) surfaces as a function of the La chemical potential ( $\mu$ , eV). It ranges from the potential of La bulk to that minus the binding energy of lanthanum hexaboride. Surface names are explained in the text. The arrows indicate the effect of relaxing the stoichiometric slabs, possibly terminated by different surfaces. For the other surfaces, only the relaxed energies are plotted. (112)La is the most stable LaB<sub>6</sub> surface. However, in nearly the whole plot, the Ba surface is even lower.

of the final or transition state one considers. Hence, several types of stability exist: toward decomposition, deformation, roughening, chemical reactions, etc. The binding energy of a compound estimates its stability toward decomposition. The anisotropy in the surface energy determines the stability toward deformation. Also, the stability toward roughening contains contributions from surfaces of other indices. In fact, lowering the energy of the surface under consideration increases its stability indiscriminately. The (relative) energy of a surface will therefore be taken as the measure of its stability.

The surface energy is calculated as the difference between the (total) energy of a slab and that of the equivalent bulk, normalized to surface area ( $A_s$ ). There is no equivalent bulk for surfaces that are part of a nonstoichiometric slab. A surface energy can be calculated, nevertheless, that varies with the chemical potential of La ( $\mu_{La}$ ), when a thermodynamic equilibrium is assumed between the bulk and reservoirs of the constituting elements. For the (001)La surface, we get:

$$\gamma^{La}(\mu_{La}) = [E_{slab} - \text{no. formula units} \cdot E_{bulk} - \mu_{La}] / 2A_s$$

The chemical potential ranges from its elemental bulk value to that value minus the binding energy of LaB<sub>6</sub>. Chemical



**Figure 13.** Surface energies ( $\gamma$ , eV/nm<sup>2</sup>) of the LaB<sub>6</sub> surfaces as a function of the lanthanum chemical potential ( $\mu$ , eV). It ranges from the potential of La bulk to that minus the binding energy of LaB<sub>6</sub>. Surface names are explained in the text. The (001)Ba surface is the most stable in nearly all the plot.

potentials can, in principle, be controlled during crystallization. In general, crystal surfaces with low energies are formed with large surface areas and vice versa. However, only the most stable one will be (thermodynamically) formed of the different terminations of the same index surface.

The surface energies of LaB<sub>6</sub> are reported in Figures 9–12 for the (001), (011), (111), and (112) surfaces, respectively. For all surfaces, the decrease in energy with structural relaxation is indicated. The relaxation energy of the (001)La surface (0.44 eV per surface unit cell) compares very well with that reported by Monnier et al.<sup>10</sup> The most stable terminations are the (001)La, the (011)La, the (111)B<sub>stoi</sub>, and the (112)La surfaces. Now, we focus on the (012) surface. The (average) surface energy of the La and B<sub>dip</sub> terminations is 22.2 eV/nm<sup>2</sup>, and both do not depend strongly on the chemical potential. They do not need to be considered further. The (012) surface with steps of [001] faces is much more stable, though.

It is depicted in Figure 13 together with the most stable surfaces of other indexes. Of these, the most stable is either the (111) surface or the (001) surface, depending on chemical potential. The (112) surface is a little more stable than the (011) surface, and the (012) surface is least stable of all.

Concerning surface adlayers, substitution of La with Ba on the (001) and (112) surfaces stabilizes those further (the chemical potential of elemental barium is taken). This is in contrast with addition of an extra layer of lanthanum. The effects are understood by realizing that the binding between lanthanums is weaker than the bond between a lanthanum and a boron atom and that barium at the surface has one few broken bond than lanthanum. The (001)Ba surface is most stable.

## 6. Conclusions

To summarize, we carried out first-principles calculations on the (001), (011), (111), (112), and (012) surfaces of lanthanum hexaboride to study the anisotropy of both the work function and the surface energy and their relationship. The different surface terminations and structural relaxation were taken into account. No reconstructions were considered, but we did include [001] steps at the (012) surface. We also studied the influence of monolayers of Ba and Cs and bilayers of La at both the (001) and the (112) surfaces. Of LaB<sub>6</sub>'s intrinsic surfaces, either the (111)B or the (001)La surface is most stable, depending on chemical potential. The latter has a very low work function of 2.07 eV. By substituting barium atoms for surface lanthanums, both the energy and the work function decrease even further.

The resulting work function and surface energy values are, respectively, 1.43 eV and  $\approx 2$  eV/nm<sup>2</sup> in the middle of the range of the chemical potential.

Let us now make contact with experiment. Our work function for the (001)La surface compares very well to that reported by Aono et al.<sup>12</sup> (2.07 vs 2.1 eV). Our work functions for the stepped (012), (011)La, and (111)B surfaces (respectively, 2.38, 2.94, and 3.98 eV) correspond reasonably to those of Oshima et al. (respectively, 2.2, 2.68, and 3.4 eV).<sup>18,19</sup> Also reproduced is the La termination of the (001) and (011) surfaces, the B termination of the (111) surface, as well as the large variation seen in polycrystalline work function: in changing the lanthanum chemical potential, a crystal with mainly (001) surfaces can be turned into one with mainly (111) surfaces (see Figure 13). The work functions of the two differ by nearly 2 eV. Moreover, both the energy and the work function of a lanthanum hexaboride surface strongly depend on its termination (and possible modifications of surface atoms), and so small surface contaminations are expected to have a strong effect. Pelletier et al.,<sup>28</sup> Chambers et al.,<sup>29</sup> and Fomenko<sup>31</sup> all confirm this.

The results on the polar metallic compound LaB<sub>6</sub> compare well to those on the intermetallics BaAl<sub>4</sub>, CaAl<sub>4</sub>, and BaAuIn<sub>3</sub>.<sup>4,5</sup> Those compounds contain metallic elements from different columns in the periodic table, and the surfaces terminating with the most electropositive elements are most stable. Moreover, their work functions are lowest and decreased with respect to their elemental values. Lanthanum hexaboride crystallizes in a decidedly different structure, and the constituting elements are from column 3 of the periodic table. One is even nonmetallic (B). As a consequence, either a La surface {(001)} or a boron surface {(111)} is most stable, depending on chemical potential. The lanthanum and boron layers at the latter surface are nearly equiplanar, and as a result, the work functions of those terminations differ least ( $\Phi = 3.26$  and 3.98 eV, respectively). We conclude that LaB<sub>6</sub> is a more complex compound; nevertheless, the generality of a stable and low work function surface still holds.

**Acknowledgment.** We thank R. Coehoorn (Philips, TU/e) for valuable suggestions. This work was part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM) with financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

## References and Notes

- (1) The concept of stability is discussed in Section 5.
- (2) *Handbook of Chemistry and Physics*; CRC: Boca Raton, FL, 1997.
- (3) Smoluchowski, R. *Phys. Rev.* **1941**, *60*, 661.
- (4) Uijtewaal, M. A.; de Wijs, G. A.; de Groot, R. A.; Coehoorn, R.; van Elsbergen, V.; Weijtens, C. H. L. *Chem. Mater.* **2005**, *17*, 3879.
- (5) Uijtewaal, M. A.; de Wijs, G. A.; de Groot, R. A. *Surf. Sci.* **2006**, *600*, 2495.
- (6) Zhang, H.; Zhang, Q.; Tang, I.; Qin, L. C. *J. Am. Chem. Soc.* **2005**, *127*, 2862.
- (7) Nakamoto, M.; Fukuda, K. *Appl. Surf. Sci.* **2002**, *202*, 289.
- (8) Marchenko, A. A.; Cherepanov, V. V.; Tarashchenko, D. T.; Kazantseva, Z. I.; Naumovets, A. G. *Surf. Sci.* **1998**, *416*, 460.
- (9) Davis, P. R.; Swanson, L. W.; Hutta, J. J.; Jones, D. L. *J. Mater. Sci.* **1986**, *21*, 825.
- (10) Monnier, R.; Delley, B. *Phys. Rev. B* **2004**, *70*, 193403.
- (11) Yamauchi, H.; Takagi, K.; Yuito, I.; Kawabe, U. *Appl. Phys. Lett.* **1976**, *29*, 638.
- (12) Aono, M.; Nishitani, R.; Oshima, C.; Tanaka, T.; Bannai, E.; Kawai, S. *J. Appl. Phys.* **1979**, *50*, 4802.
- (13) Mogren, S.; Reifengerger, R. *Surf. Sci.* **1991**, *254*, 169.
- (14) Waldhauser, W.; Mitterer, C.; Laimer, J.; Stori, H. *Surf. Coat. Technol.* **1998**, *98*, 1315.
- (15) Kawanowa, H.; Souda, R.; Otani, S.; Ikeuchi, T.; Gotoh, Y.; Stracke, P.; Krischok, S.; Kemper, V. *Surf. Sci.* **2001**, *482*, 250.
- (16) Takigawa, T.; Sasaki, I.; Meguro, T. *J. Appl. Phys.* **1982**, *53*, 5891.

- (17) Nishitani, R.; Aono, M.; Tanaka, T.; Oshima, C.; Kawai, S.; Iwasaki, H.; Nakamura, S. *Surf. Sci.* **1980**, *93*, 535.
- (18) Oshima, C.; Bannai, E.; Tanaka, T.; Kawai, S. *J. Appl. Phys.* **1977**, *48*, 3925.
- (19) Oshima, C.; Aono, M.; Tanaka, T.; Nishitani, R.; Kawai, S. *J. Appl. Phys.* **1980**, *51*, 997.
- (20) Gesley, M.; Swanson, L. W. *Surf. Sci.* **1984**, *146*, 583.
- (21) Swanson, L. W.; Gesley, M. A.; Davis, P. R. *Surf. Sci.* **1981**, *107*, 263.
- (22) Fomenko, V. S. *Powder Metall. Met. Ceram.* **1997**, *36*, 335.
- (23) Samsonov, G. V.; Kondrashov, A. I.; Okhremchuk, L. N.; Podchernyaeva, I. A.; Siman, N. I.; Fomenko, V. S. *J. Less-Common. Met.* **1979**, *67*, 415.
- (24) Kuznetsov, G. I.; Sokolovsky, E. A. *Phys. Scr.* **1997**, *T71*, 130.
- (25) Yutani, A.; Kobayashi, A.; Kinbara, A. *Appl. Surf. Sci.* **1993**, *70–71*, 737.
- (26) Ebihara, K.; Hiramatsu, S. *Rev. Sci. Instrum.* **1996**, *67*, 2765.
- (27) Baikie, I. D.; Peterman, U.; Lagel, B.; Dirscherl, K. *J. Vac. Sci. Technol. A* **2001**, *19*, 1460.
- (28) Pelletier, J.; Pomot, C. *Appl. Phys. Lett.* **1979**, *34*, 249.
- (29) Chambers, S. A.; Davis, P. R.; Swanson, L. W. *Surf. Sci.* **1982**, *118*, 93.
- (30) Danielsen, L. R. *J. Appl. Phys.* **1981**, *52*, 300.
- (31) Fomenko, V. S. *Powder Metall. Met. Ceram.* **1995**, *34*, 329.
- (32) Zhang, H.; Tang, J.; Zhang, Q.; Zhao, G.; Yang, G.; Zhang, J.; Zhou, O.; Qin, L. C. *Adv. Mater.* **2006**, *18*, 87.
- (33) Watson, R. E.; Perlman, M. L. *Surf. Sci.* **1982**, *122*, 371.
- (34) Kohn, W. *Rev. Mod. Phys.* **1999**, *71*, 1253.
- (35) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.
- (36) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, R558.
- (37) Kresse, G.; Hafner, J. *Phys. Rev. B* **1994**, *49*, 14251.
- (38) Kresse, G.; Furthmüller, J. *Comput. Mater. Sci.* **1996**, *6*, 15.
- (39) Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953.
- (40) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758.
- (41) Louie, S. G.; Froyen, S.; Cohen, M. L. *Phys. Rev. B* **1982**, *26*, 1738.
- (42) Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, *13*, 5188.
- (43) Booth, C. H.; Sarrao, J. L.; Hundley, M. F.; Cornelius, A. L.; Kwei, G. H.; Bianchi, A.; Fisk, Z.; Lawrence, J. M. *Phys. Rev. B* **2001**, *63*, 224302.
- (44) Topor, L.; Kleppa, O. J. *J. Chem. Thermodyn.* **1984**, *16*, 993.
- (45) Meschel, S. V.; Kleppa, O. J. *J. Alloys Compd.* **2001**, *321*, 183.
- (46) Technically, the stoichiometric slabs in the [001] and [112] direction are formed by two different boron surfaces. However, neither their work function nor their surface energies play a role of importance. Therefore, their differences will be ignored.
- (47) Van der Heide, P. A. M.; Ten Cate, H. W.; Ten Dam, L. M.; De Groot, R. A.; De Vroomen, A. R. *J. Phys. F: Met. Phys.* **1986**, *16*, 1617.
- (48) Kubo, Y.; Asano, S. *Phys. Rev. B* **1989**, *39*, 8822.
- (49) Fall, C. J.; Binggeli, N.; Baldereschi, A. *Phys. Rev. Lett.* **2002**, *88*, 156802.
- (50) Fall, C. J.; Binggeli, N.; Baldereschi, A. *J. Phys.: Condens. Matter* **1999**, *11*, 2689.
- (51) Aono, M.; Tanaka, T.; Bannai, E.; Oshima, C.; Kawai, S. *Phys. Rev. B* **1977**, *16*, 3489.